

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08K 13/02 // (C08K 13/02, 3:26, 5:521)		A1	(11) International Publication Number: WO 00/05304
			(43) International Publication Date: 3 February 2000 (03.02.00)
(21) International Application Number: PCT/US99/16411			(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
(22) International Filing Date: 20 July 1999 (20.07.99)			
(30) Priority Data: 60/093,588 21 July 1998 (21.07.98) US			
(71) Applicant (for all designated States except US): FMC CORPORATION [US/US]; 1735 Market Street, Philadelphia, PA 19103 (US).			
(72) Inventors; and (75) Inventors/Applicants (for US only): PAPAOGLOU, Elizabeth, S. [US/US]; 1075 Victory Drive, Yardley, PA 19067 (US). KOTAK, Jay [US/US]; 35 Hamilton Lane, South, Plainsboro, NJ 08536 (US).			
(74) Agent: PINTZUK, Marcia, D.; FMC Corporation, 1735 Market Street, Philadelphia, PA 19103 (US).			Published With international search report.
(54) Title: METHOD FOR REDUCING ODOR DURING PROCESSING OF FLAME RETARDANT POLYMERS			
(57) Abstract <p>A method for reducing the odor formed during thermal processing of a thermoplastic polymer composition containing a tris(trihaloneopentyl) phosphate flame retardant additive is disclosed. The method comprises processing a polymer composition containing the thermoplastic polymer, the flame retardant additive, and a quantity of a hydrotalcite effective to reduce the odor formed during processing at an elevated temperature. The method is especially suited for processing polymers that must be processed above 230 °C, such as polypropylene, polybutylene terephthalate, and polycarbonate.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

TITLE**METHOD FOR REDUCING ODOR DURING PROCESSING
OF FLAME RETARDANT POLYMERS**CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application claims priority from U.S. Provisional Application 60/093,588, filed July 21, 1998.

TECHNICAL FIELD

10 This invention relates to methods for reducing the odor formed during processing of polymers that comprise a tris(trihaloneopentyl)phosphate flame retardant additive. In particular, this invention relates to reducing odor by adding a hydrotalcite to the polymer.

15

BACKGROUND OF THE INVENTION

Thermoplastic polymers can be modified by a number of flame retardant additives that either hinder ignition and/or reduce flame spread. In many of these applications
20 it is preferred or mandatory to incorporate an additive into the polymer to improve its flame resistance or retardance. Although addition of flame retardant additives improves the flame retardant properties of polymers, flame retardant additives can adversely affect the physical
25 properties of the polymer and may also make it more difficult to process the polymer.

Tris(trihaloneopentyl) phosphates, particularly tris(tribromoneopentyl) phosphate, are useful as flame
retardant additives. These additives are melt blendable
30 into many thermoplastic polymers and have minimal effect on the properties and processing of the polymer. Their exceptional heat stability produces materials with

processing and storage stability. However, use these additives has been limited by a tendency for polymers incorporating them to develop objectionable odors, especially when processed at higher temperatures. An objectionable odor may also be produced if the residence time of the polymer in the heated portion of the extruder used to process the polymer/flame retardant additive composition is prolonged for any reason. The processing temperature referred to in this disclosure is the melt temperature of the polymer. The temperature of the polymer in the extruder is typically higher than temperature of the barrel of the extruder because of the force exerted on the polymer during extrusion heats the polymer above the barrel temperature.

Although tris(trihaloneopentyl) phosphates are useful as flame retardant additives in thermoplastic polymers, such as polypropylene, they less acceptable if the polymer is to be processed at a temperature of 260°C than if it is processed at a temperature of 230°C. These materials have not been widely used in polymers such as polyesters, which are almost always processed at temperatures in excess of 250°C. Thus, a need exists for a method for controlling the odor produced when polymer compositions comprising tris(trihaloneopentyl) phosphate flame retardant additives, particularly tris(tribromoneopentyl) phosphate, are processed at temperatures in excess of 230°C, and especially above 250°C or 260°C.

SUMMARY OF THE INVENTION

We have discovered that the incorporation of a hydrotalcite into a polymer comprising tris(trihaloneo-

pentyl) phosphate flame retardant additive reduces objectionable odors during processing, even at temperatures in excess of 250°C.

5 Miyata, U.S. Pat. 4,729,854 [EP 129,805] describes compositions comprising a thermoplastic resin, a halogen containing organic flame retardant additive and a hydrotalcite. The hydrotalcite is stated to effective in neutralizing any hydrogen halides involved during the processing of the resin. Although not being bound by any theory or explanation, it is believed that in the instant invention the hydrotalcite reacts with neutral tetrahalide and possibly other odoriferous residuals, thus reducing the odor. The effectiveness of the hydrotalcite in reducing the odor associated with a neutral halogenated species is 15 surprising.

In one aspect the invention is a method for reducing the odor formed during the processing a thermoplastic polymer composition comprising a tris(trihaloneopentyl) phosphate flame retardant additive at elevated temperature. 20 The method comprises processing the thermoplastic polymer composition at a temperature of at least 230°C, typically at least 250°C or 260°C; in which the thermoplastic polymer composition comprises a thermoplastic polymer, a tris(trihaloneopentyl) phosphate flame retardant additive, 25 and a quantity of a hydrotalcite effective to reduce the odor formed during processing at the elevated temperature.

In another aspect the invention is a thermoplastic polymer composition comprising at least one thermoplastic polymer, at least one tris(trihaloneopentyl) phosphate flame retardant additive, and at least one hydrotalcite, in 30 which the amount of the hydrotalcite present is effective

to reduce the odor formed during processing at an elevated temperature.

A preferred tris(trihaloneopentyl) phosphate flame retardant is tris(tribromoneopentyl) phosphate. Preferred thermoplastic polymers are polypropylene, polyethylene, copolymers of propylene and ethylene, and mixtures and blends thereof. In a preferred embodiment the composition additionally comprises a flame retardant additive synergist, preferably antimony trioxide; a co-additive halogenated flame retardant additive having at least one halogen atom attached to an aliphatic carbon atom as part of its molecular structure, preferably tetrabromobisphenol-A-bis(2,3-dibromopropyl)ether and/or tetrabromobisphenol-S-bis(2,3-dibromopropyl)ether; and, optionally and preferably, a metallocene elastomer in an amount effective to prevent blooming of the tris(trihaloneopentyl)phosphate flame retardant additive.

DISCLOSURE OF THE INVENTION

The tris(trihaloneopentyl) phosphate flame retardant additive comprises one or more of tris(trichloroneopentyl) phosphate; tris(dichlorobromoneopentyl) phosphate; tris(chlorodibromoneopentyl) phosphate and tris(tribromoneopentyl) phosphate. The preferred phosphate flame retardant additive is tris(tribromoneopentyl) phosphate. Although tris(tribromoneopentyl) phosphate offers the optimum flame retardant performance, it is more prone to the evolution of objectionable odors.

The nature of the polymer, the degree of flame retardancy desired or required, the cost of the polymer, the costs of the various additives, the intended use for the flame retardant polymer, the presence or absence of

WO 00/05304

other flame retardant additives and/or synergists, and the value in use of the flame retardant polymer are all factors that may influence the quantity of flame retardant additive or additives used. Generally, the compositions comprise 5 from 1 to 20 parts by weight, preferably from 2 to 15 parts by weight, and most preferably from 3 to 10 parts by weight of tris(trihaloneopentyl) phosphate flame retardant additive.

The compositions may comprise any thermoplastic 10 polymer or any mixture or blend of two or more such polymers. Examples of polymers which are useful include polyolefins, especially polypropylene and polyethylene, polystyrene, polyvinyl fluoride, polyvinyl chloride, poly- 15 vinylidene fluoride, polyvinylidene chloride, polytetrafluoroethylene, polychlorotrifluoroethylene, polyacrylonitrile, polymethyl methacrylate, polyoxymethylene, polyphenylene oxide, polyphenyl sulfide, polycarbonate, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polycaprolactone (nylon 6), polyhexamethylene 20 adipamide (nylon 6/6), epoxy resins, polyurethanes and cellulose acetate, or any mixture of two or more thereof. The preferred polymers are polyolefins, polycarbonate, and polyesters, such as PET and PBT.

The polyolefins (sometimes called "polyolefin resins") 25 may be derived from a variety of monomers, especially propylene, ethylene, butene, iso-butylene, pentene, hexene, heptene, octene, 2-methyl propene, 2-methyl butene, 4-methylpentene, 4-methyl hexene, 5-methyl hexene, bicyclo-(2,2,1)-2-heptene, butadiene, pentadiene, hexadiene, 30 isoprene, 2,3-dimethyl butadiene, 3,1-methyl pentadiene, 1,3,4-vinyl cyclohexene, vinyl cyclohexene, cyclopentadiene, and the like. The polyolefins include copolymers

produced from any of the foregoing monomers and the like, and include homopolymer blends, copolymer blends, homopolymer-copolymer blends, and blends containing minor amounts (less than 50 wt%) of one or more styrenic monomers or polymers, such as styrene and methylstyrene.

The preferred polyolefins are polypropylene and polyethylene, including atactic, syndiotactic and isotactic polypropylene and polyethylene, low density polyethylene, high density polyethylene, ultra-high density polyethylene, and linear low density polyethylene; block copolymers of ethylene and propylene; and random copolymers of ethylene and propylene. These polyolefins may be produced using a variety of processes known to those skilled in the art and are available from a variety of sources. The polymers may have a range of melt indexes (MI), but will typically have MI values in the range 0.5 to 30. The most preferred polyolefin is polypropylene.

Hydrotalcite compounds are layered double hydroxide compounds, which may be obtained from synthetic or natural sources. Preferably the hydrotalcite is a compound that satisfies the formula $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ or the formula $\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot 3\text{H}_2\text{O}$ (this formula has also been written as $6\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_2 \cdot 12\text{H}_2\text{O}$). In its ionic form hydrotalcite may be written as $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}]^{2+}[\text{CO}_3]^{2-}$.

Hydrotalcites are commercially available from J.M. Huber under the brand name Hysafe® 539 or from Reheis under the brand name of L-55RII. These are multilayered minerals comprising primarily a magnesium/aluminum hydroxy carbonate having a formula approximating to $\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13} \cdot 5\text{H}_2\text{O}$.

The amount of hydrotalcite incorporated into the thermoplastic polymer may vary through a wide range, from 0.001 to 5.0 parts by weight, preferably from 0.01 to 1.0

parts by weight, based on 100 parts by weight of thermoplastic polymer. The amount of hydrotalcite used is generally proportional to the amount of phosphate flame retardant additive present. The ratio of the weight of
5 phosphate flame retardant additive to the weight of hydrotalcite is normally in the range 40:1 to 3:1, preferably 20:1 to 6:1.

The hydrotalcite is preferably dispersed evenly through the polymer. The hydrotalcite normally has an
10 average particle size of 1 to 10 microns, preferably 1 to 5 microns. Surface treatments, such as those disclosed in Miyata, U.S. Pat. 4,729,854, may be used, but are not essential.

The compositions preferably comprise a conventional
15 anti-oxidant. Although the hydrotalcite reduces or eliminates the noxious odors formed during processing of a polymer comprising a tris(trihaloneopentyl) phosphate, the polymer may become discolored during the processing step. However, discoloration may be reduced by incorporating an
20 anti-oxidant, preferably a phenolic anti-oxidant, into the composition. Other classes of anti-oxidants, such as amines, thioesters and phosphites may also be useful.

A wide range of phenolic anti-oxidants are known. These anti-oxidants, such as those described in
25 Thermoplastic Polymers and Additives - Theory and Practice John T Lutz, Jr., ed, Marcel Dekker, 1989, are all potentially useful. Representative phenolic antioxidants include: 2,6-di-t-butyl-4-methylphenol, 2,6-di-t-butyl-4-sec-butylphenol, octadecyl 3,5-di-t-butyl-4-hydroxy-
30 cinnamate, 2,2-ethylidenebis-(4,6-di-t-butylphenol), 2,2-methylenebis(4-methyl-6-t-butylphenol), 4,4-butyldienebis(6-t-butyl-m-cresol), 4,4-methylenebis(2,6-di-t-butyl-

phenol), 1,3,5-tris(4-*t*-butyl-3-hydroxy-2,6-dimethyl-
benzyl) *s*-triazine-2,4,6-(1*H*,3*H*,5*H*)trione, tetrakis-
(methylene-3-[3,5-di-*t*-butyl-4-hydroxyphenyl]propionate)-
methane, 2,2-oxamidobisethyl-3(3,5-di-*t*-butyl-4-hydroxy-
5 phenyl)propionate, 1,6-hexamethylenebis(3,5-di-*t*-butyl-4-
hydroxyhydrocinnamate), 1,3,5-trimethyl-2,4,6-tris(3,5-di-
t-butyl-4-hydroxybenzyl)-benzene, tris(2-methyl-4-hydroxy-
5-*t*-butylphenyl)butane, 1,3,5-tris(3,5-di-*t*-butyl-4-
hydroxybenzyl)isocyanurate, 3,5-di-*t*-butyl-4-hydroxy-
10 cinnamic acid triester with 1,3,5-tris(2-hydroxyethyl)-*s*-
triazine-2,4,6-(1*H*,3*H*,5*H*)trione, and *N,N*-hexamethylene-
bis(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate).

Each of these may be useful, either alone or in
combination with one or more other anti-oxidants, to reduce
15 or eliminate discoloration during processing. However,
these anti-oxidants may exert an antagonistic effect when
used in the presence of the hydrotalcite and reduce the
effectiveness with which it decreases the odor formation.
This tendency is preferably minimized or avoided by routine
20 experimentation designed to optimize the both choice of
phenolic anti-oxidant(s) and the quantity used.

Typically polyolefins comprise a synergist for the
flame retardant additive. Useful synergists include
antimony trioxide, sodium antimonate, antimony pentoxide,
25 zinc stannate, zinc hydroxystannate, zinc borate, and any
mixtures of two or more thereof. Preferred synergists are
antimony trioxide and zinc borate. In general the ratio of
the weight of tris(trihaloneopentyl) phosphate flame
retardant additive to the weight of synergist will be in
30 the range 3:1 to 1:1, typically 2:1.

The compositions may also comprise various other
additives, such as photostabilizers, thermal stabilizers,

antistatic and nucleating agents, pigments, fillers, glass, and other materials known in the art.

A preferred combination of additives for use in polyolefins, especially in polypropylene, propylene/-
5 ethylene copolymers, and mixtures and blends thereof, is disclosed in Papazoglou, WO 98/17718, incorporated herein by reference. The composition comprises: the polyolefin, preferably polypropylene; 3 to 10% by weight of at least one tris-(trihaloneopentyl)phosphate flame retardant
10 additive, preferably tris-(tribromoneopentyl)phosphate; 0.5 to 5% of a co-additive halogenated flame retardant additive having at least one halogen atom attached to an aliphatic carbon atom as part of its molecular structure, preferably tetrabromobisphenol-A-bis(2,3-dibromopropyl)ether or tetra-
15 bromobisphenol-S-bis(2,3-dibromopropyl)ether; and a flame retardant additive synergist selected from the group consisting of antimony trioxide, antimony pentoxide, zinc stannate, sodium antimonate, zinc hydroxystannate, and zinc borate, preferably antimony trioxide, in which the ratio of
20 the weight of antimony trioxide to the total weight of the tris(trihaloneopentyl)phosphate and the co-additive is about 1:5 to 1:1. The processing of these compositions may produce an offensive odor, which is reduced or eliminated by incorporating a hydrotalcite into the composition.

25 Compositions that comprise a polyolefin and a polar additive, particularly a polar flame retardant additive, such as tris(trihaloneopentyl) phosphate, may suffer from a tendency for the additive to "bloom" from the composition, i.e., to form a sticky exudate upon the surface of the
30 composition. [A polar flame retardant additive is one that is polar relative to the polyolefin.] Addition of metallocene elastomers to polyolefins containing polar

flame retardant additives produces a composition that resists blooming even at high heat aging temperatures.

"Metallocene elastomers" are substantially linear ethylene/C₃-C₂₀ α -olefin copolymers, especially

5 substantially linear ethylene/C₅-C₁₀ α -olefin copolymers, prepared by constrained geometry catalysis using metallocene catalysts, such as are disclosed in McKay, U.S. Patent No. 5,747,580, and Chum, U.S. Patent 5,677,383. These materials typically have an ultimate elongation of

10 700% or greater. Any metallocene elastomer that is compatible with the selected polyolefin is useful. Preferably it does not degrade the properties of the polyolefin. Preferred metallocene elastomers are α -octene/ethylene elastomers.

15 Metallocene elastomers are available from DuPont Dow, Wilmington, DE, as the Engage® elastomers, such as Engage® 8180 elastomer and Engage® 8403 elastomer. These materials have: densities of about 0.863 g/cm³ to about 0.913 g/cm³; melt flow indices of about 0.5 dg/min to about 30 dg/min;

20 differential thermal analysis melting peaks of about 49°C to about 107°C; ultimate tensile strengths of about 4.1 MPa to about 33.8 MPa; and ultimate elongations of about 700% to greater than 1000%.

Processing of compositions comprising a polyolefin, a

25 tris(trihaloneopentyl) phosphate flame retardant additive, and a metallocene elastomer may produce an offensive odor, which can be reduced or eliminated by incorporating a hydrotalcite into the composition. The amount of elastomer used should be an amount effective to yield an improvement

30 in the bloom resistance of the polymer. Typically, such amounts are about 2 to 5 parts by weight of the elastomer

per 100 parts by weight of polyolefin. However, up to about 20 parts by weight of elastomer, preferably up to 15 parts by weight of elastomer, may be added to reduce blooming under severe conditions, such as heating at 100°C for seven days.

The effectiveness of any particular elastomer may vary depending upon the polyolefin and flame retardant or retardants selected. In addition, the selection of a specific elastomer will also depend upon the particular application specifications. Elastomers having the requisite properties for optimization of bloom inhibition and good physical performance may be selected by routine testing.

The compositions may be compounded using techniques well known in the art. A uniform composition is desirable if the optimum flame retardant additive performance is to be obtained. The use of a twin screw extruder is preferred to the use of a single screw extruder. It is also desirable to keep the extrusion temperature above the melting points of the polyolefin, the flame retardant additives, and any other additives. The extrusion temperature should not be so high as to accentuate the difference between the viscosities of the polyolefin and the additives.

The polymer compositions containing flame retardant additives are often formulated as concentrates, known as "masterbatches," comprising the polymer from 15 to 50% by weight of the tris(trihaloneopentyl) phosphate flame retardant additive, and a proportionate amount of the other additives. The concentrates are "diluted" with additional quantities of polymer prior to the processing step. However, the tendency to form obnoxious odors is greater in

this type of procedure and the invention finds particular application in the preparation of master batches.

INDUSTRIAL APPLICABILITY

5 The invention finds particular applications in processes by which polymers are fabricated into finished articles by molding processes. The invention also finds particular application in the formulation of polypropylene compositions and polyethylene terephthalate compositions
10 used to form fibers. Tris(tribromoneopentyl) phosphate has not been used in polyethylene terephthalate fibers because of its tendency produce objectionable odors during processing. Fiber extrusion is carried out at relatively high temperature (250°C - 280°C) and involves high shear
15 forces being applied to a polymer as well as a polymer having a high surface area. All these factors tend to exacerbate the problem of odor formation. Addition of hydrotalcite to the composition alleviates this problem, even when these elevated extrusion temperatures are used.
20 The advantageous properties of this invention can be observed by reference to the following examples which illustrate, but do not limit, the invention.

EXAMPLES

Glossary

25

Hysafe® 539 Hydrotalcite (J.M Huber, Borger, TX)

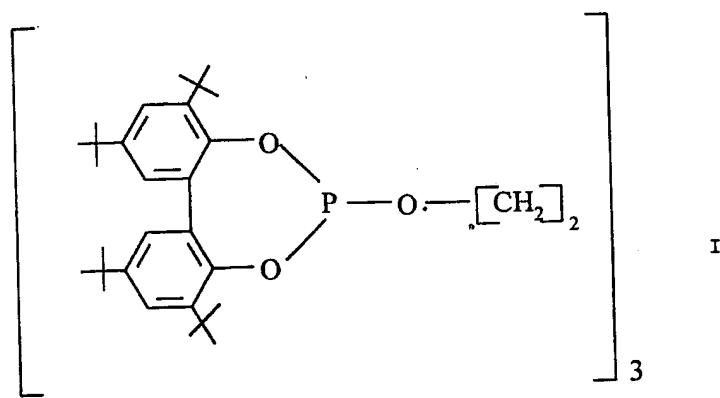
30

Irgafos® 168 Tris(2,4-di-*t*-butylphenyl)phosphite (Ciba Additives, Ardsley, NY)

Irganox® 1010 Tetrakis[methylene (3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)methane (Ciba Additives, Ardsley, NY)

35

- LC21FF Anti-oxidant comprising about $\frac{1}{3}$ Irganox® 1010 and $\frac{2}{3}$ Irgafos® 12, a phosphite anti-oxidant having Formula I (Ciba Additives, Ardsley, NY)
- 5 Profax 6523 Polypropylene homopolymer (MI 12) (Montell Polyolefins)
- 10 Rynite® Thermoplastic polyethylene terephthalate resin (DuPont, Wilmington, DE)



Example 1

- 15 Polypropylene compositions were prepared in a base polymer containing Profax 6523 polypropylene resin (100 parts by weight), tris(tribromoneopentyl) phosphate (4 parts by weight), and antimony trioxide (2 parts by weight). The other components are shown in Table 1.
- 20 The compositions were flood fed into a Haake 19" (about 48 cm) conical twin screw extruder operated at 70 rpm. The temperature profile was 210°C at the barrel (3 zones total) and 210°C at the die. The melt temperature measure with a melt thermometer was 230-240°C (depending on
- 25 measurement at the beginning or towards the end of the run). The stranded material was passed through a 6 ft (about 1.83 M) cooling water bath at a temperature of about

10°C. The strands were pelletized and collected. The pelletized materials were allowed to dry overnight until all surface moisture had evaporated.

The compositions were extruded in a Randcastle RCP-0625 extruder operated at 10 rpm with a single stand die at a melt temperature of 250-260°C. The extruder was closely monitored by the operator, who recorded the intensity of any odor involved during the processing operation. The results are summarized in Table 1.

10 The compositions obtained from the Haake extruder were heat aged to simulate long residence time during molding of complicated articles. About 25 g of each composition was placed in an aluminum weighing cup and the cups placed in a recirculating oven. Three tests were run at temperatures
15 of 200, 240 and 250°C measured by a thermocouple placed in the middle of the oven. The odor generated was judged subjectively. At 200°C, all materials had slight or no odor. At 240°C or 250°C, the odor matched the odor observed during the processing of the same compositions through the
20 Randcastle extruder.

Table 1
Processing of Polypropylene at 230-240°C^a

	Hysafe® 539	Irganox® 1010	LC21FF	Odor
1				Strong
2	0.002			No Odor
3	0.002		0.005	Some Odor
4	0.002	0.005		Slight Odor
5	0.002	0.005	0.005	Odor
6	0.001	0.0025	0.0025	Slight Odor

^aIn Profax 6523 polypropylene resin (100 parts by weight),
 tris(tribromoneopentyl) phosphate (4 parts by weight), and
 5 antimony trioxide (2 parts by weight).

Example 2

The polymer compositions indicated in Table 2 were prepared and processed into fibers. F5-372 is a high
 10 purity grade of the phosphate of Example 1. The compositions were precompounded in a Haake extruder with a melt temperature of 250°C (barrel temperature 230°C). The material was then flood fed into a Randcastle extruder RCP-0625 operated at 4 rpm. The die was a single strand die.
 15 The results are shown in Table 2.

TABLE 2
Rynite® PET Processed into Fibers at 280°C^a

	1	2	3	4
FG-372	-	0.1	0.2	0.1
Hysafe® 539	-	-	-	0.005
Irganox® 1010	-	-	-	.01
Odor	None	Strong	Strong	None

^aMelt temperature during fiber extrusion.

20

Having described the invention, we now claim the following and their equivalents.

CLAIMS

What is claimed is:

- 5 1. A method for reducing the odor formed during processing of a thermoplastic polymer composition at elevated temperature, the method comprising:
 processing the thermoplastic polymer composition at a temperature of at least 230°C;
- 10 in which:
 the thermoplastic polymer composition comprises a thermoplastic polymer, a tris(trihaloneopentyl) phosphate flame retardant additive, and a quantity of a hydrotalcite effective to reduce the odor formed during processing at
15 the elevated temperature.
2. The method of claim 1 in which the tris(trihaloneopentyl) phosphate flame retardant additive is tris(tribromoneopentyl) phosphate.
- 20 3. The method of claim 1 or claim 2 in which the thermoplastic polymer composition is processed at a temperature in excess of 260°C.
- 25 4. The method of any of the preceding claims in which the thermoplastic polymer is a polyolefin.
- 30 5. The method of claim 4 in which the polyolefin is selected from the group consisting of polypropylene, polyethylene, copolymers of propylene and ethylene, and mixtures thereof.

6. The method of either claim 4 or 5 in which in that the polyolefin is processed so as to form polyolefin fibers.

5 7. The method of any of claims 1 to 4 in which the polymer composition comprises polyethylene terephthalate.

8. The method of any of claims 1 to 3 in which the thermoplastic polymer is polybutylene terephthalate.

10

9. The method of any of claims 1 to 3 in which the thermoplastic polymer is a polycarbonate.

10. The method of any of the preceding claims in which the polymer composition comprises from 1 to 20 parts of the tris(trihaloneopentyl) phosphate flame retardant additive per 100 parts by weight of the thermoplastic polymer.

20 11. The method of claim 10 in which the polymer composition comprises from 2 to 15 parts by weight of the tris(tribromoneopentyl) phosphate flame retardant additive.

25 12. The method of any of the preceding claims in which the polymer composition comprises from 0.001 to 5.0 parts by weight of a hydrotalcite.

30 13. The method of claims 12 in which the hydrotalcite has an average particle size from 1 to 10 microns.

14. The method of any of the preceding claims in which the polymer composition comprises a phenolic antioxidant.

5 15. A composition comprising at least one thermoplastic polymer, at least one tris(trihaloneopentyl) phosphate flame retardant additive and at least one hydrotalcite, in which the amount of the hydrotalcite present is effective to reduce the odor formed during
10 processing at an elevated temperature.

16. The composition of claim 15 in which the tris(trihaloneopentyl) phosphate flame retardant additive is tris(tribromoneopentyl) phosphate.
15.

17. The composition of claim 15 or claim 16 in which the thermoplastic polymer is a polyolefin.

18. The composition of claim 17 in which the
20 polyolefin is selected from the group consisting of polypropylene, polyethylene, copolymers of propylene and ethylene and mixtures thereof.

19. The composition of claim 18 in which the
25 composition comprises 3 to 10% by weight of the tris-(trihaloneopentyl)phosphate flame retardant additive; 0.5 to 5% of a co-additive halogenated flame retardant additive having at least one halogen atom attached to an aliphatic carbon atom as part of its molecular structure; and a flame
30 retardant additive synergist selected from the group consisting of antimony trioxide, antimony pentoxide, zinc stannate, sodium antimonate, zinc hydroxystannate, and zinc

borate, in which the ratio of the weight of antimony trioxide to the total weight of the tris(trihaloneopentyl)-phosphate flame retardant additive and the co-additive is about 1:5 to 1:1.

5

20. The composition of claim 19 additionally comprising a metallocene elastomer in an amount effective to prevent blooming of the tris(trihaloneopentyl)phosphate flame retardant additive.

10

21. The composition of claim 15 or 16 in which the thermoplastic polymer is polyethylene terephthalate.

22. The composition of claim 15 or 16 in which the
15 thermoplastic polymer is polybutylene terephthalate.

23. The composition of claim 15 or 16 in which the thermoplastic polymer is a polycarbonate.

20 24. The composition of any of claims 15 to 18 and 20-23 comprising from 1 to 20 parts by weight of the tris(trihaloneopentyl) phosphate flame retardant additive.

25 25. The composition of claim 24 comprising from 2 to 15 parts by weight of the tris(tribromoneopentyl) phosphate flame retardant additive.

26. The composition of any of claims 15 to 25
30 comprising from 0.001 to 5.0 parts by weight of a hydrotalcite.

27. The composition of claim 26 in which the hydrotalcite has an average particle size of from 1 to 10 microns.

5 28. The composition of any of claims 15 to 27 additionally comprising a phenolic anti-oxidant.

29. A mater batch for a flame and bloom resistant composition comprising:

- 10 (a) a polyolefin;
- (b) a total of at least 25% by weight of at least one tris(trihaloneopentyl) phosphate flame retardant additive;
- (c) at least one metallocene elastomer; and
- 15 (d) hydrotalcite;

 in which the ratio of the weight of phosphate flame retardant additive to the weight of hydrotalcite is about 20:1 to 6:1.

INTERNATIONAL SEARCH REPORT

International Application No.

PC1/US 99/16411

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K13/02 /// (C08K13/02, 3:26, 5:521)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 129 805 A (KYOWA CHEM IND CO LTD) 2 January 1985 (1985-01-02) cited in the application page 3, line 1 - line 9 claims 1-5	1-28
A	EP 0 464 782 A (VISKASE CORP) 8 January 1992 (1992-01-08) claims 1-17	1-28
A	DATABASE WPI Section Ch, Week 199507 Derwent Publications Ltd., London, GB; Class A17, AN 1995-048956 XP002120330 & JP 06 329843 A (TONEN KAGAKU KK), 29 November 1994 (1994-11-29) abstract	1-28

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

26 October 1999

Date of mailing of the international search report

05/11/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Siemens, T

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/16411

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0129805	A	02-01-1985	JP 1619704 C	30-09-1991
			JP 2038107 B	29-08-1990
			JP 60001241 A	07-01-1985
			CA 1258335 A	08-08-1989
			DE 3468887 A	25-02-1988
			ES 533455 A	16-04-1986
			US 4729854 A	08-03-1988
EP 0464782	A	08-01-1992	AT 143857 T	15-10-1996
			AU 638845 B	08-07-1993
			AU 7946991 A	09-01-1992
			CA 2043301 A,C	04-01-1992
			DE 69122553 D	14-11-1996
			DE 69122553 T	15-05-1997
			ES 2094774 T	01-02-1997
			FI 913213 A	04-01-1992
			JP 1980400 C	17-10-1995
			JP 4232740 A	21-08-1992
			JP 7002405 B	18-01-1995
			NO 176789 B	20-02-1995
			NZ 238304 A	25-06-1993
			PT 98189 A	29-05-1992
			US 5290613 A	01-03-1994
JP 6329843	A	29-11-1994	NONE	